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INTERNATIONAL ISOCYANATE INSTITUTE, INC.

REACTION OF TDI WITH WATER AND WITH WET SAND

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1. INTRODUCTION.

The increasing use of isocyanates has prompted many questions regarding the safety of these materials during transport. Observations made following an accident to a rail tanker, during which a considerable amount of TDI was spilt onto a marshy woodland terrain, led to a research programme to examine possible procedures and practical countermeasures in such situations.

Model experiments were set up, in order to investigate the behaviour of TDI after soaking into the earth or escaping into water. In these, TDI was maintained in contact with both stagnant and running water and with wet sand.

The answers to three main questions were sought:-

1. How long does it take for TDI to be decomposed into polyureas by water?
2. In the above reaction are appreciable quantities of toluylene diamine (TDA) formed?
3. After how long can a contaminated area be declared safe?

The information contained in this report is available for use during any discussions with authorities concerned with accidents involving spillage of TDI.

2. EXPERIMENTAL.

All experiments were carried out at room temperature, i.e. the TDI was always present in liquid form.

2.1 Stagnant water.

In this experiment, the behaviour of TDI in stagnant water was simulated by placing 20 litres of water in a glass container 20 x 40 x 30 cm (i.e. 24 litres full capacity) and adding 0.5 litres of TDI (80/20) to it. On account of its greater specific gravity, the TDI settled in a layer on the bottom of the container.

Tests were carried out at pH values of 5, 7 and 9 (Expts. C, D and E respectively) and also, out of scientific curiosity, at pH 1 (Expt.B). The pH values were adjusted by means of HCl or NaOH and checked with a glass electrode.

2.2 Running water (Expt.A).

20 litres of water were placed in a glass vessel as above and 0.5 litres TDI added thereto. A system of tubes was arranged so that a continuous flow of water occurred (2000 litres per day, i.e. 100 changes daily). Streamline flow was maintained, so that no TDI or polyurea was removed mechanically.

### 2.3 Wet Sand.

These experiments simulated the covering of a spillage of TDI with wet sand.

5 kg of TDI were placed in a container of 30 litres and covered with 55 kg of wet sand (50 kg sand and 5 kg water). The total depth of the mixture was about 38 cm, 10 cm of which represented the depth of TDI originally added. The sand used was of a type in general use for absorbing or covering spilt liquids, oil, etc. The container was left uncovered at room temperature. At weekly (later, monthly) intervals, samples were taken from half-way down the mixture, and analysed for TDI and TDA.

This experiment (Expt.F) showed that, by the time the first sample had been taken (after 1 week), almost the whole of the TDI had been already converted to polyurea. A further experiment (Expt.G) was, therefore, set up in which samples were taken daily. A coarse-grained sand was used in this test and two samples were taken for analysis each time, from the upper and lower regions of the mixture.

### 3. ANALYTICAL.

#### 3.1 Determination of TDA.

At intervals of a few days, 50 ml samples of the aqueous phase were taken from Experiments A-E, adjusted to pH 2 with HCl and extracted with 2 x 50 ml ether in a separating funnel. This extraction served to remove neutral material which can interfere with the subsequent determination of amines by thin layer chromatography (TLC). The aqueous phase was then adjusted to pH 11 with NaOH solution and again extracted with 2 x 50 ml ether. These combined extracts, after concentrating to 5 ml (for a limit of detection of 0.1 ppm) or 0.5 ml (0.01 ppm limit), were then subjected to analysis by TLC in comparison with known standard solutions.

The experiments with wet sand were subjected to a similar procedure.

The results of these analyses are given in Table 1.

#### 3.2 Determination of TDI.

##### 3.2.1 By TLC (Expts.A-E).

A hard, compact crystalline crust was first formed at the interface between the TDI and the supernatant water. After a few days the crystal formation continued downwards, and after about 30 days the liquid TDI had practically disappeared. The crystalline mass at the bottom of the container was removed after 35 days, dried over calcium chloride in a desiccator and thoroughly mixed in a mortar. In order to determine the amount of TDI remaining, a sample was immediately taken, treated with nitro-reagent (Keller, Dunlop & Sandridge, Anal.Chemistry 46, (12), 1845, Oct.1974), and subsequently subjected to TLC in comparison with standard solutions. The results are given in Table 2.



### 3.2.2. By colorimetry (Expts. F & G).

After 1-2 days, the sand in Expts. F and G had assumed a white appearance, indicating the commencement of polyurea formation. The reaction continued without any noticeable external signs, except for a slow and steady evolution of carbon dioxide. After 5 months, Expt. F was discontinued; Expt. G was terminated after 8 days. No appreciable solidification of the mass had occurred in either case.

At various intervals samples were taken from the reaction mixture. Any TDI still unreacted was hydrolysed to amine (TDA) by means of a mixture of glacial acetic and sulphuric acids. The 2:4- and 2:6-toluylene diamines were coupled with p-toluyldiazonium chloride to give colours which were measured in a photometer at 470 nm (Heuser, Reusche, Wrabetz & Fauss, Z.analyt.Chem. 257, (2), 119 (1971)). The results are shown in Table 3.

## 5. DISCUSSION.

### 5.1 TDA.

Tests for TDA in the experiments with running water (Expt. A) and with wet sand (Expts. F & G) show barely detectable (<0.01 ppm) amounts present. In the case of the stagnant water tests (Expts. C, D and E), an examination of the mean values shows an increasing concentration of TDA as the pH is also increased, e.g. at pH 5, TDA = ca. 0.6 ppm.  
pH 7, TDA = ca. 0.7 ppm.  
pH 9, TDA = ca. 1.0 ppm.

The concentration of TDA appears to be independent of the duration of the experiment. Experiment B (at pH 1, included for comparison only) gave, as expected, a relatively high TDA concentration (mean = 19 ppm).

Not too much importance should be attached to the rise in TDA concentration with rising pH value, although this cannot be explained completely. The mean value of all the measurements made at pH 5, 7 and 9 result in a concentration of only 0.77 ppm. If one imagines a 10 tonne leakage of TDI which is substantially covered with water then, after a sufficient time, only ca. 8 g of TDA will be formed, a quantity which in this context may be regarded as negligible from a toxicological point of view.

### 5.2 TDI.

In the case of Experiments A, C, D & E (stagnant and running water) the TDI had reacted with the water almost completely after 1 month. This can be expected in practice, provided that the TDI remains in the liquid state. The reaction will doubtless be slowed down if the temperature of the TDI falls below its solidification point (12.5-13.5°C.).

Covering spilt TDI with wet sand appears to be a very good method of:-

- a) minimising the direct consequences of a significant TDI leakage, and
- b) achieving a relatively rapid conversion to polyurea.

Although the experiment with wet sand has shown that a small percentage of unreacted TDI is still retained, it is noteworthy how quickly TDI reacts with water in the presence of sand (about 1 week).

There is, as yet, no indication that polyureas formed by TDI can be attacked by micro-organisms in the soil. A conclusive answer to this question is likely to be obtained in the near future as a result of the work being carried out by Prof. Domsch at Braunschweig. If it is indeed shown that the reaction products of TDI and water are inert, it may be reasonably claimed that the treatment of large leakages of TDI with water and sand is a sufficient treatment where, because of the extent of the leakage or for other reasons, treatment with the normal decontaminant is not feasible. Also, the removal of the contaminated sand or earth to a special place of disposal would appear unnecessary under such circumstances.

TABLE 1 : FORMATION OF TDA.

a) In stagnant (Expts.B-E) or running water (Expt.A).

Sample taken after X days	Expt:	TDA (ppm w/w)				
		A	B pH 1	C pH 5	D pH 7	E pH 9
0		(0.4)*	3	1	(0.01)*	0.3
2		< 0.01	7	0.8	0.4	0.5
5		< 0.01	33	0.3	0.8	0.3
7		< 0.01	12	0.3	0.9	0.5
9		< 0.01	15	0.3	0.8	1
12		< 0.01	25	0.4	0.8	2.5
14		< 0.01	20	0.3	0.7	1.5
16		< 0.01	25	0.5	0.7	2
19		< 0.01	25	0.8	0.8	1.5
21		< 0.01	16	0.7	0.8	1
23		< 0.01	18	0.9	0.8	0.7
25		< 0.01	22	0.7	0.7	0.7
27		< 0.01	15	0.6	0.6	0.7
32		< 0.01	25	0.4	0.4	0.8
34		< 0.01	22	0.5	0.5	0.4

\* These results not included in calculating mean values.

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